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(54) Vinyl acetate resin emulsion composition.

(57) Vinyl acetate resin emulsion composition produced by the addition of a water soluble compound having alcoholic OH group during emulsion-polymerization or emulsion-copolymerization reaction to vinyl acetate resin emulsion which is obtained by emulsion-polymerization or emulsion-copolymerization of vinyl acetate under the presence of polyvinyl alcohol.

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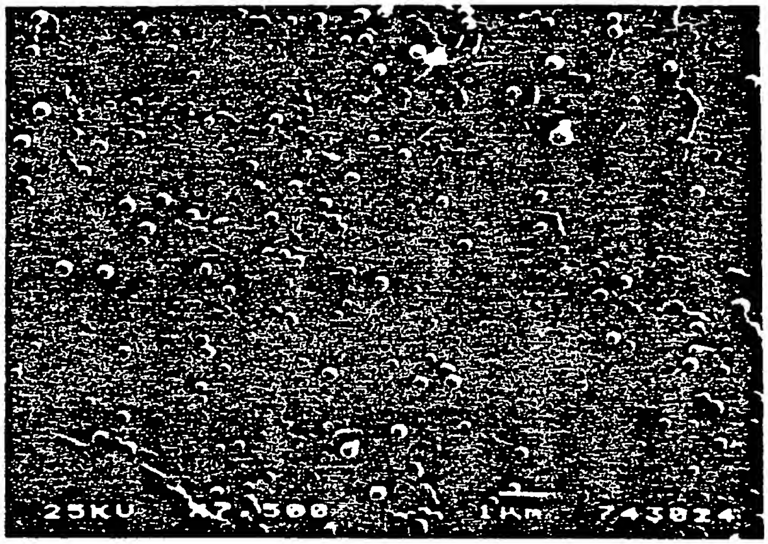
FIG. 1



Vinyl acetate resin emulsion composition

This invention relates to vinyl acetate resin emulsion composition outstanding in features such as excellent workability, heat r sistance, water resistance, storage life, etc.

Vinyl acetate resin emulsion obtained by the emulsion polymerization of vinyl acetate monomer, using water soluble high polymer such as polyvinyl alcohol as the protective colloid, has been widely used for adhesives, paint and for finishing paper and fibers.

Vinyl acetate resin emulsion used so widely, however, is not free from various faults. Some of these faults are; (1) the viscosity is temperature dependent, i.e., it increases significantly in winter time when the temperature is low, and makes it difficult to use the emulsion since the emulsion is inferior in the workability, (2) the viscosity also significantly increases at high solids content which also makes it difficult for processing, (3) separation and sedimentation occurs at low solids content and decreases the storage life, (4) the use of water soluble high polymer such as polyvinyl alcohol as the protective coloid causes low water resistance of the resulting film.

It is an object of the present invention to eliminate such various faults inherent to vinyl acetate resin emulsion and to make resin emulsion composition with excellent workability, heat and water resistance and storage life available. Furthermore, the vinyl acetate resin emulsion composition of the present invention comprises vinyl acetate resin emulsion, produced by emulsion-polymerizing or -copolymerizing vinyl acetate in the presence of polyvinyl alcohol, to which a water soluble compound having alcoholic OH group is added during emulsion-polymerization or -copolymerization reaction.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

Figs. 1 to 4 are the electron micrographs showing the particle structures of emulsion compositions of Examples 1 to 4, i.e., four vinyl acetate resin emulsion compositions of the present invention, and

Figs. 5 to 9 are the electron micrographs showing the particle structures of emulsions of comparative Examples 2 to 6, i.e., five vinyl acetate resin emulsions.

The water soluble compound with alcoholic OH group to be contained in the composition of the present invention (hereinafter called "the compound") may be any substance so long as it does not inhibit or prohibit emulsion polymerization or copolymerization but, generally, the following substances are used. The examples of monohydric alcohol are:

Methanol: CH_3OH, Ethanol: CH_3CH_2OH, Isopropanol: $CH_3CH(OH)CH_3$, Tertiary butanol: $CH_3C(CH_3)_2OH$.

The examples of glycol are:

Ethylene glycol: $C_2H_4(OH)_2$, propylene glycol: $HOC_2H_3(CH_3)OH$, diethylene glycol: $HOC_2H_4OC_2H_4OH$, triethylene glycol: $HOC_2H_4OC_2H_4 \cdot OC_2H_4OH$, hexylene glycol: $HO(CH_3)C_3H_3(CH_3)_2OH$, trimethylene glycol: $C_3H_6(OH)_2$, 3-methyl-1, 3-butanediol: $CH_3C(CH_3)OHCH_2CH_2OH$.

The examples of glycol ether are:

Ethylene glycol monomethyl ether: $CH_3OC_2H_4OH$, ethylene glycol monoethyl ether: $C_2H_5OC_2H_4OH$, ethylene glycol monobuthyl ether: $C_4H_9OC_2H_4OH$, diethylene glycol monomethyl ether: $CH_3O(C_2H_4O)_2H$, diethylene glycol monobuthyl ether: $C_4H_9OC_2H_4OC_2H_4OH$, propylene glycol monomethyl ether: $CH_3OC_3H_6OH$, propylene glycol monoethyl ether: $C_2H_5OC_3H_6OH$, ethylene glycol mono-tertiary-buthyl ether: $(CH_3)_3COCH_2CH_2OH$, 3-methoxy-1-butanol: $CH_3CH(OCH_3)CH_2OH_2OH$, 3-methyl-3-methoxy butanol: $CH_3OC(CH_3)_2CH_2CH_2OH$.

The examples of polyglycols are:

Polyethylene glycol of average molecular weight of 200, 300, 400, 600, 1000 or 1500: $HO(CH_2CH_2O)_nCH_2CH_2OH$.

The water soluble property as mentioned of the present invention means that 100g of compound of the present invention dissolved in 100cc of 20°C water does not separate or precipitate even if the compound is left to stand.

In the case of composition according to the present invention, the preferable amount of the compound to be added is 0.5-15% by weight based on vinyl acetate resin emulsion. The effect will be too small when the compound is less than 0.5% by weight, and, will result in the unstable composition of emulsion if the compound exceeds 15%. Therefore, 0.5 to 15% by weight should be most suitable in practice.

The compound should be added to vinyl acetate resin emulsion during the polymerization process of vinyl acetate. No effect can be expected if the compound is added after the polymerization process is completed. The emulsion polymerization condition of vinyl acetate for obtaining vinyl acetate resin emulsion composition of the present invention is not subjected to any particularly specified conditions and, with

regard to time and temperature for polymerization and the way to add vinyl acetate monomer, it can be carried out in accordance with generally known conditions.

The vinyl acetate resin emulsion composition of the present invention, for example, can be obtained by charging water, polyvinyl alcohol and the compound into a reactor equipp d with an agitator, thermometer, dropping device and reflux condenser and, then, after heating and dissolving the content, adding vinyl acetate monomer and polymerization catalyst at adequate temperature, and emulsion-polymerizing the content for several hours. pH adjuster such as ammonium carbonate or tartaric acid or reducing agent such as Na-formaldehydesulfoxylate or L-ascorbic acid may also be present in the polymerization system when necessary.

Vinyl acetate for producing the composition of the present invention can be either only vinyl acetate monomer, or mixture of vinyl acetate monomer and other polymerizable monomers such as vinyl propionate, acrylic ester, methacrylic ester, etc. In other words, the vinyl acetate resin emulsion used in the present invention can be obtained either by emulsion polymerization or emulsion copolymerization.

For producing the composition of the present invention, polyvinyl alcohol with polymerization degree of 100 to 4,500 and saponification value not less than 65 mol% for normal application may be preferably used. It can also be modified polyvinyl alcohol such as carboxyl modified polyvinyl alcohol. It may also be used, if necessary, simultaneously with anionic, cationic or nonionic surfactant normally in use. For the emulsion polymerization or copolymerization catalyst to produce the composition of the present invention, persulfate such as potassium persulfate, ammonium persulfate or peroxide such as hydrogen peroxide or a redox catalyst combined the above mentioned peroxide and reducing agents are suitable.

The outstanding features of the vinyl acetate resin emulsion composition of the present invention are believed to originate from the following reasons; the compound have favorable properties as a dispersant which facilitates emulsion polymerization and, moreover, the particle structure of the resultant vinyl acetate resin emulsion, in comparison with that of conventional emulsion, is such that the particles are moderately dispersed, not adhering to each other, and the particle sizes of the emulsion are as small as 0.2 to 0.4 µm against 0.5-1.0 µm of conventional emulsion. The compound therefore serves as a good solvent for polyvinyl alcohol and vinyl acetate resin, unlike the conventional solvents and plasticizers.

As mentioned above, the vinyl acetate resin emulsion composition of the present invention sustains low viscosity even at high concentration and shows less increase of viscosity in winter time as, when compared with conventional types of emulsion, the particle sizes are smaller or less than 0.5 µm, and have less tendency of aggregating to each other.

Therefore, the composition of the present invention, when applied as an adhesive, has excellent strength and heat resistance and, when used as paint, fiber, ceramic binder, and for finishing papers, has an excellent binding property.

Examples 1 - 4 and Comparative Examples 1 - 6

54.9g of water, 4g of polyvinyl alcohol having a saponification value of 88 mol% and a polymerization degree of 1700 (Trade name Kuraray POVAL 217 of Kuraray Co., Ltd.), 5g of any kind of compound used in the present invention as shown in Table 1 and 0.1g of ammonium carbonate have been charged into a reactor equipped with agitator, thermometer, dropping device and reflux condenser. It was then heated to 80 °C while being stirred for 30 minutes to dissolve the contents. 1g of 10% water solution of ammonium persulfate and 35g of vinyl acetate monomer were added by slowly dropping into it over three to four hours. After this drop charging, the contents were then cooled after being aged for 30 minutes at the same temperature as above. The vinyl acetate resin emulsion composition thus produced by emulsion-polymerizing vinyl acetate monomer has been tested for viscosity, water resistance of the dry film and solids content and the results are shown in Table 1. For comparison purposes, the viscosity, water resistance and solids content have been tested of the vinyl acetate resin emulsion produced in the same manner as Examples 1 - 4, except that the compound used in Examples 1 - 4 was replaced with water-insoluble dibutyl phthalate (DBP), (Comparative Example 5), and also of commercial vinyl acetate resin emulsion (Trade name Bond CH_{18} of Konishi Co., Ltd.), (Comparative Example 6), in the same manner and the results are also shown in Table 1.

Furthermore, 54.9g of water, 4g of polyvinyl alcohol and 0.1g of the same ammonium carbonate as Examples 1 - 4, have been charged into the same reactor as the above. It was then heated to 80 °C while being stirred for 30 minutes to dissolve the contents. 1g of 10% water solution of ammonium persulfate and 35g of vinyl acetate monomer were added by slowly dropping into it for four hours. After the drop charging, the contents were then aged for 30 minutes at th same temperatur as above. Vinyl acetat resin emulsion

(Comparative Examples 2 - 4) obtained by adding 5g of various types of compounds used in the present invention as shown in Table 1 and thorough stirring and cooling has been tested for viscosity, water resistanc and solids cont nt in the sam manner as above, and the results are shown in Table 1. (Comparative Example 1 could not be tested as it was gelled during the emulsifying process).

Electron microscopic tests have been made on the particle structure of the vinyl acetate resin emulsion compositions as shown in Exampl s 1 - 4, using JEOL Ltd.'s scanning electron microscope JSM-T220 and the results are shown in Figs. 1 - 4 (all in 1:7,500 magnification).

For comparison purposes, the particle structure of the emulsion of Comparative Examples 2 - 6 have also been tested using said electron microscope and the results are shown in Figs. 5 - 9 (all in 1:7,500 magnification.)

By comparing Figs. 1 - 4 with Figs. 5 - 9, it becomes apparent that the particle sizes are smaller and particles have less tendency of adhering to each other and more favorably dispersing in the vinyl acetate resin emulsion composition of the present invention than in the vinyl acetate resin emulsion of Comparative Examples 2 - 4 which has been produced by adding the compound used in the present invention after the completion of emulsion polymerization and also in the conventional vinyl acetate resin emulsion as the Comparative Examples 5 - 6.

Table 1

Items \ Examples		1	2	3	4
Compound		Isopropyl alcohol	3-methyl-1,3-butanediol	3-methoxy-1-butanol	Polyethylen glycol of av. moledular weight 200
Viscosity (cps)	30°C	3,250	5,500	3,600	6,000
	0°C	12,025	13,200	12,600	24,000
Increase in Viscosity (times)		3.7	2.4	3.5	4.0
Water resistance (second)		180 or more	180 or more	180 or more	180 or more
Solids content (%)		39.0	43.2	43.0	43.5
Particle size (μm)		0.2 - 0.4	0.2 - 0.4	0.2 - 0.4	0.2 - 0.4

(continued)

Items / Comparative Examples		1	2	3	4	5	6
Compound		Isopropyl alcohol	3-methyl-1,3-butanediol	3-methoxy-1-butanol	Polyethylene glycol of av. moledular weight 200	DBP	Bond CH_{18}
Viscosity (cps)	30°C	Gelled and unable to measure	9.050	8,600	9,700	49,000	31,000
	0°C	Gelled and unable to measure	36,200	35,260	40,740	250,000	155,000
Increase in Viscosity (times)		-	4.0	4.1	4.2	5.1	5.0
Water resistance (second)		-	90	90	120	40	50
Solids content (%)		-	43.3	43.2	43.7	43.1	40.5
Particle size (μm)		-	0.5 - 0.7	0.5 - 0.7	0.5 - 0.9	0.5 - 0.7	0.5 - 0.8

Note: 1) Using a Brookfield type viscometer. "0°C" means that the viscosities of samples were measured by after they had been left in a refrigerator at 0°C for 24 hours.

2) It shows the ratio between the viscosities at 30°C and 0°C.

3) Emulsion composition was spread over a glass plate to form a continuous 0.2 mm thick film and left at room temperature (20°C) for 3 days. The glass plate was then placed horizontally and in close contact over a piece of newspaper with the film facing upward on which a drop of 20°C water was dropped and the time, upon lapse of which 8-point "Hiragana" types below the wet film became illegible, was measured.

4) After leaving 1g. of emulsion in a 100°C oven for 60 minutes, it was measured while leaving it in a desiccator.

5) It was measured from electron micrographs.

As apparent from the results shown in Table 1, the emulsion composition of the present invention obtained from Examples 1 - 4 are significantly lower in the viscosity and also the viscosity was less dependent on temperature than in the case of conventional vinyl acetate resin emulsion as Comparative Examples 2 - 6. Furthermore, with regard to the water resistance, types were sufficiently legible even after 180 seconds in the case of the emulsion of the present invention whereas in the case of the conventional vinyl acetate emulsion of Comparative Examples 2 - 6 types became illegible after 40 to 120 seconds. As apparent from these results, the emulsion composition of the present invention is superior in its water resistance.

Examples 5 - 10 and Comparative Example 7

In these Examples, water of the respective amount as shown in Table 2 together with polyvinyl alcohol, ethylene glycol monotertiary butylether and ammonium carbonate of the amount as shown in Table 2 have been charged in the same type of reactor as used for Examples 1 - 4. The contents were heated to 80°C while being stirred for 30 minutes to dissolve the contents. 10% water solution of ammonium persulfate and vinyl acetate monomer in the amount as shown in Table 2 were added by dropping for 4 hours and aged for 30 minutes at the same temperature as above after the drop charging, and then cooled.

The vinyl acetate resin emulsion composition thus produced by emulsion polymerizing acetate vinyl monomer in the above mentioned process has been tested for viscosity and solids content by the same manner as applied to Examples 1 - 4 and the results are shown in Table 2.

For comparison purposes, the vinyl acetate resin emulsion (Comparative Example 7) produced in the same manner as Example 5, except that ethyleneglycol monotertiary butylether was replaced by water, has been tested in the same manner as Example 5 for the respective viscosity and solids content and the results are also shown in Table 2.

Table 2

Item		Examples						Comparative Examples	
		5	6	7	8	9	10	7	5
Water (g)		59.4	58.9	56.9	54.9	49.9	44.9	59.9	54.9
Polyvinyl alcohol (g)		4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Ammonium carbonate (g)		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
10% Water Solution of Ammonium persulfate (g)		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Vinyl acetate monomer (g)		35.0	35.0	35.0	35.0	35.0	35.0	35.0	35.0
Ethylene glycol monotertiary butyl ether (g)		0.5	1.0	3.0	5.0	10.0	15.0	0	DBP 5.0
Total (g)		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Solids content (%)		39.2	40.3	41.0	42.8	48.3	49.0	38.7	43.1
Viscosity	30° C	9,000	8,250	10,700	6,250	3,400	3,200	10,750	49,000
(cps)	0° C	37,8000	33,000	34,240	15,625	8,160	7,680	48,375	250,000
Increase in Viscosity (times)		4.2	4.0	3.2	2.5	2.4	2.4	4.5	5.1

As apparent from the results shown in Table 2, the emulsion composition of the present invention as Examples 5 - 10 is significantly lower in the viscosity and the viscosity is less temperature dependent when compared with the conventional vinyl acetate resin emulsion of Comparative Example 7.

Moreover, the bond strength at high temperature (60° C) was compared between the emulsion composition of Example 8 and the emulsion of Comparative Example 5. The bond strengths at high temperature (60° C) of both emulsions were measured immediately after taking them out from 60° C dryer after leaving them in it for one hour. The measurement has been made according to the process stipulated in JIS (Japanese Industrial Standard) K6804. The results have shown that the bond strength at high temperature (60° C) of the emulsion composition of Example 8 was 44 kg/cm^2 and superior to that of the conventional emulsion of Comparative Example 5, which was 32 kg/cm^2.

<u>Example 11 and Comparative Example 8</u>

38.9g of water, 4g of carboxyl modified polyvinyl alcohol having a saponification value of 80 mol% and a polymerization degree of 600 (Trade name Kuraray POVAL KL506 of Kuraray Co., Ltd.), 5g of 3-methoxy-1-butanol and 0.1g of ammonium carbonate have been charged into the same reactor as the one used for Examples 1 - 4. It was then heated to 75° C while being stirred for 30 minutes to dissolve the contents. 1g of 10% water solution of ammonium persulfate was and, further, 51g of vinyl acetate monomer was added by slowly dropping into it for five hours. After the drop charging, the contents were then cooled after being aged for 30 minutes at the same temperature as above. The vinyl acetate resin emulsion composition thus produced by emulsion-polymerizing vinyl acetate has been tested for viscosity and solids content in the same manner as Examples 1 - 4 and the results are shown in Table 3.

For comparison purposes, the viscosity and solids content have been tested of the vinyl acetate resin emulsion (Comparative Example 8) produced in the same manner as Example 11, except for replacing 3-methoxy-1-butanol by DBP, and the results are shown in Table 3.

Table 3

		Example 11	Comparative Example 8
Viscosity	30° C	38,000	149,000
(cps)	0° C	76,000	387,400
Increase in Viscosity (times)		2.0	2.6
Solids content (%)		59.8	59.7

As apparent from the results shown in Table 3, the emulsion composition of the present invention, i.e., Example 11, is less dependent on temperature than the conventional emulsion of Comparative Example 8.

Furthermore, when the emulsion composition of Example 11 has been thinnly coated on the surface of a piece of lauan plywood by a glass rod, it was possible to coat easily since the viscosity was relatively low despite its high (59.8%) concentration (solids content).

The conventional emulsion of Comparative Example 8, in contrast, could not be coated easily because of its high viscosity.

Example 12 and Comparative Examples 9 - 10

45.8g of water, 4g of polyvinyl alcohol having a saponification value of 88 mol% and a polymerization degree of 500 (Trade name Kuraray POVAL 205 of Kuraray Co., Ltd.), 5g of ethylene glycol monotertiary butyl-ether and 0.1g of tartaric acid have been charged into the same reactor as the one used for Examples 1 - 4. It was then heated to 80° C while being stirred for 30 minutes to dissolve the contents. 0.1g of hydrogen peroxide was then added and, further, 35g of vinyl acetate monomer was added by slowly dropping into it for two hours. The contents were then added with 20g of water and cooled after being aged for 30 minutes at the same temperature as above. The vinyl acetate resin emulsion composition thus produced by emulsion-polymerizing vinyl acetate has been tested for viscosity and solids content in the same manner as Examples 1 - 4 and the results are shown in Table 4. Moreover, the storage life of the emulsion composition thus obtained has been tested by leaving it in a 200cc of glass bottle under room temperature (20° C), the results of which are shown in Table 4.

Meanwhile, 35.8g of water, 4g of polyvinyl alcohol having a saponification value of 88 mol% and a polymerization degree of 500 (Trade name Kuraray POVAL 205 of Kuraray Co., Ltd.), 5g of dibutyl phthalate (DBP) and 0.1g of tartaric acid have been charged into a reactor. It was then heated to 80° C while being stirred for 30 minutes to dissolve the contents. 0.1g of hydrogen peroxide was then added and, further, 35g of vinyl acetate monomer was added by slowly dropping into it for four hours. The contents were then added with 20g of water and cooled after being aged for 30 minutes at the same temperature as above. The vinyl acetate resin emulsion (Comparative Example 9) thus produced by emulsion-polymerizing vinyl acetate has been tested for viscosity, solids content and storage life for comparison purposes and the results are shown in Table 4.

In addition, the viscosity, solids content and storage life of commercial vinyl acetate resin emulsion (Trade name Bond CH 3000L of Konishi Co., Ltd.) (Comparative Example 10) have been measured in the same manner as above for comparison purposes and the results are shown in Table 4.

Table 4

	Example 12	Comparative Example 9	Comparative Example 10
Viscosity (cps) 30°C	150	310	520
Solids content (%)	39.0	39.8	40.8
Storage life	No changes after 3 months	Separation & sedimentation observed after 1 month	Separation & sedimentation observed after 1 month

As apparent from Table 4, as compared with Comparative Examples 9 and 10, no irregularity such as separation and sedimentation has been observed after three months in the emulsion composition of Example 12 of the prevent invention despite its low viscosity. Hence, the emulsion composition showed good storage life. In contrast, separation and sedimentation were observed in the conventional vinyl acetate resin emulsion of Comparative Examples 9 and 10 after one month.

Example 13 and Comparative Examples 11 - 12

45.8g of water, 4g of polyvinyl alcohol having a saponification value of 88 mol% and a polymerization degree of 500 (Trade name Kuraray POVAL 205 of Kuraray Co., Ltd.), 5g of 3-methyl-3-methoxybutanol and 0.1g of tartaric acid have been charged into the same reactor as the one for Examples 1 - 4. It was then heated to 75°C while being stirred for 30 minutes to dissolve the contents. 0.1g of hydrogen peroxide was then added and, further, 35g of vinyl acetate monomer was added by slowly dropping into it for two hours. The contents were then added with 20g of water and cooled after being aged for 30 minutes at the same temperature as above. The vinyl acetate resin emulsion composition thus produced by emulsion-polymerizing vinyl acetate has been tested for viscosity and solids content in the same manner as Examples 1 - 4 and the results are shown in Table 5.

Meanwhile, 35.8g of water, 4g of polyvinyl alcohol having a saponification value of 88 mol% and a polymerization degree of 500 (Trade name Kuraray POVAL 205 of Kuraray Co., Ltd.), 5g of dibutyl phtalate (DBP) and 0.1g of tartaric acid have been charged into a reactor. It was then heated to 75°C while being stirred for 30 minutes to dissolve the contents. 0.1g of hydrogen peroxide was then added and, further, 35g of vinyl acetate monomer was added by slowly dropping into it for two hours. The contents were then added with 20g of water and cooled after being aged for 30 minutes at the same temperature as above. The vinyl acetate resin emulsion (Comparative Example 11) thus produced by emulsion-polymerizing vinyl acetate has been tested for viscosity and solids content for comparison purposes and the results are shown in Table 5.

Furthermore, commercial vinyl acetate resin emulsion (Trade name Bond CH3000L of Konishi Co., Ltd.) (Comparative Example 12) has also been tested for viscosity, solids content and storage life for comparison and the results are shown in Table 5.

Table 5

	Example 13	Comparative Example 11	Comparative Example 12
Viscosity (cps) 30° C	150	300	500
Solids content (%)	39.1	39.9	40.0
Storage life	No changes after 3 months	Separation & sedimentation observed after 1 month	Separation & sedimentation observed after 1 month

As apparent from Table 5, as compared with Comparative Examples 11 and 12, no irregularity such as separation and sedimentation has been observed after three months in the emulsion composition of Example 13 of the prevent invention despite its low viscosity. Hence, the emulsion composition showed good storage life. In contrast, separation and sedimentation were observed in the conventional vinyl acetate resin emulsion of Comparative Examples 11 and 12 after one month.

Example 14 and Comparative Examples 13

55.8g of water, 4g of the same polyvinyl alcohol as the one used for Examples 1 - 4, and 0.1g of ammonium carbonate have been charged into the same reactor as the one used in Examples 1 - 4. It was then heated to 80° C while being stirred for 30 minutes to dissolve the contents. A mixture of 1g of 10% water solution of ammonium persulfate, 30g of vinyl acetate monomer and 5g of ethylene glycol monotertiary buthyl ether was added by slowly dropping into it for four hours. After drop charging, the contents were emulsion-copolymerized by slowing adding 5g of butyl acrylate at the same temperature and cooled after aged for 30 minutes at the same temperature as above. By testing the vinyl acetate resin emulsion composition thus obtained by emulsion-copolymerizing vinyl acetate and butyl acrylate for viscosity by the same manner as Examples 1 - 4, it was found to be 6,000 cps at 30° C. For comparison purposes, the vinyl acetate resin emulsion (Comparative Example 13) thus obtained by the same manner as Example 14, except for replacing ethylene glycol monotertiary butyl ether by DBP, was tested for viscosity in the same manner as Examples 1 - 4, and the viscosity was found to be 10,600 cps at 30° C.

As apparent from the comparison between Example 14 and Comparative Example 13, the emulsion composition of the present invention has shown significantly lower viscosity than the conventional product of Comparative Example 13 even when produced by emulsion-copolymerization by adding a mixture of vinyl acetate monomer and ethylene glycol monotertiary butyl ether to the polymerization system.

The vinyl acetate resin emulsion composition of the present invention has the following excellent characteristics:

(1) The viscosity is less temperature dependent, the viscosity increase at a lower temperature range is very little and offers good workability,

(2) It has sufficient ability to form film at low temperature without the aid of plasticizer such as DBP and the film thus produced is relatively strong and has good heat resistance,

(3) Low viscosity product can be available even at a high solids content and offers good workability,

(4) No separation and sedimentation occurs after a long period of storage at low viscosity and offers good storage life,

(5) Dry film obtained from the emulsion composition has good water resistance, and

(6) Particles of the emulsion composition are much smaller than those of conventional emulsion, and particles of the emulsion composition do not aggregate and are uniformly dispersed, therefore, the emulsion composition of the present invention offers outstanding features such as excellent binding property as a binder. The above-mentioned characteristics of the emulsion composition of the present invention are not available with the conventional vinyl acetate resin emulsion.

It renders the emulsion composition of the present invention extremely effective as adhesive for wood, paper and inorganic materials and also as a binder for water paint, paper coating material, dust-proof coating material, coating material for huge heap of coal dust, sand, short fib rs, c ramic powder, etc.

Claims

1. Vinyl acetate resin emulsion composition comprising vinyl acetate resin emulsion, produced by emulsion-polymerizing or emulsion-copolymerizing vinyl acetate in the presence of polyvinyl alcohol, to which a water soluble compound having alcoholic OH group is added during emulsion-polymerization or emulsion-copolym rization reaction.

2. Vinyl acetate resin emulsion composition according to claim 1, characterized in that said water soluble compound having alcoholic OH group is monohydric alcohol.

3. Vinyl acetate resin emulsion composition according to claim 1, characterized in that said water soluble compound having alcoholic OH group is glycol.

4. Vinyl acetate resin emulsion composition according to claim 1, characterized in that said water soluble compound having alcoholic OH group is glycolether.

5. Vinyl acetate resin emulsion composition according to claim 1, characterized in that said water soluble compound having alcoholic OH group is polyglycol.

6. Vinyl acetate resin emulsion composition according to claim 2, characterized in that monohydric alcohol is selected from the group consisting of methanol, ethanol, isopropanol and tertiarybutanol.

7. Vinyl acetate resin emulsion composition according to claim 3, characterized in that glycol is selected from the group consisting of ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, hexylene glycol, trimethylene glycol and 3-methyl-1,3-butanediol.

8. Vinyl acetate resin emulsion composition according to claim 4, characterized in that glycolether is selected from the group consisting of ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monoethyl ether, ethylene glycol monotertiary butyl ether, 3-methoxyl-butanol and 3-methyl-3-methoxybutanol.

9. Vinyl acetate resin emulsion composition according to claim 5, characterized in that polyglycol is polyethylene glycol of average molecular weight 200, 300, 400, 600, 1000 or 1500.

10. Vinyl acetate resin emulsion composition according to claim 1, characterized in that vinyl acetate is a mixture of vinyl acetate monomer and other monomer which is copolymerizable with said vinyl acetate monomer.

11. Vinyl acetate resin emulsion composition according to claim 10, characterized in that other monomer is monomer selected from the group consisting of vinyl propionate, acrylic ester and methacrylic ester.

12. Vinyl acetate resin emulsion composition according to claim 1, characterized in that the added ratio of the water soluble compound having alcoholic OH group to said vinyl acetate resin emulsion is 0.5 - 15% by weight.

13. Vinyl acetate resin emulsion composition according to claim 1, characterized in that the polyvinyl alcohol is modified polyvinyl alcohol.

14. Vinyl acetate resin emulsion composition according to claim 13, characterized in that the modified polyvinyl alcohol is carboxyl modified polyvinyl alcohol.

15. Vinyl acetate resin emulsion composition according to claim 1, characterized in that the polyvinyl alcohol has a polymerization degree of 100 - 4500 and a saponification value of not less than 65 mol%.

16. Vinyl acetate resin emulsion composition according to claim 1, characterized in that the polyvinyl alcohol is a combination of polyvinyl alcohol and surfactant.

17. Vinyl acetate resin emulsion composition according to claim 1, characterized in that the vinyl acetate resin emulsion is a product obtained by emulsion-polymerizing or emulsion-copolymerizing vinyl acetate under the presence of polymerizing catalyst selected from the group consisting of persulfate, peroxide and redox catalyst.

18. Vinyl acetate resin emulsion composition according to claim 17, characterized in that the vinyl acetate resin emulsion is a product obtained by emulsion-polymerizing or emulsion-copolymerizing vinyl acetate under the presence of at least one of the elements selected from the group consisting of pH adjuster and reducing agents.

FIG. 1

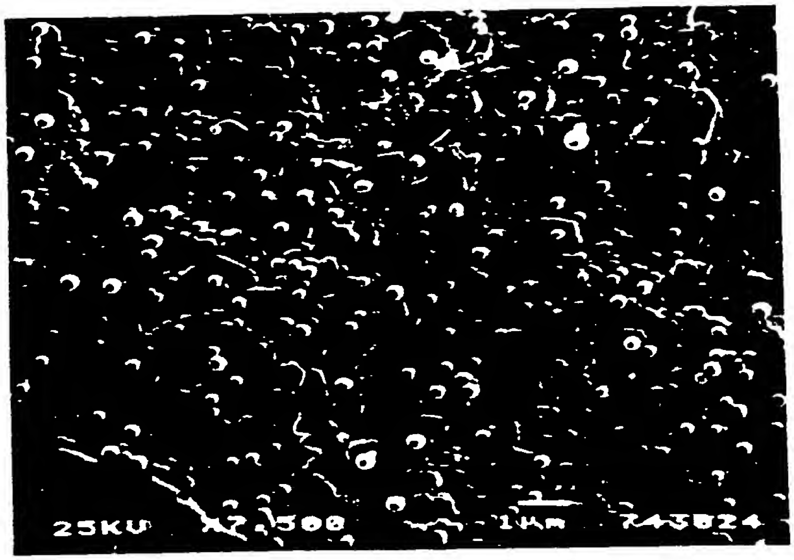


FIG. 2

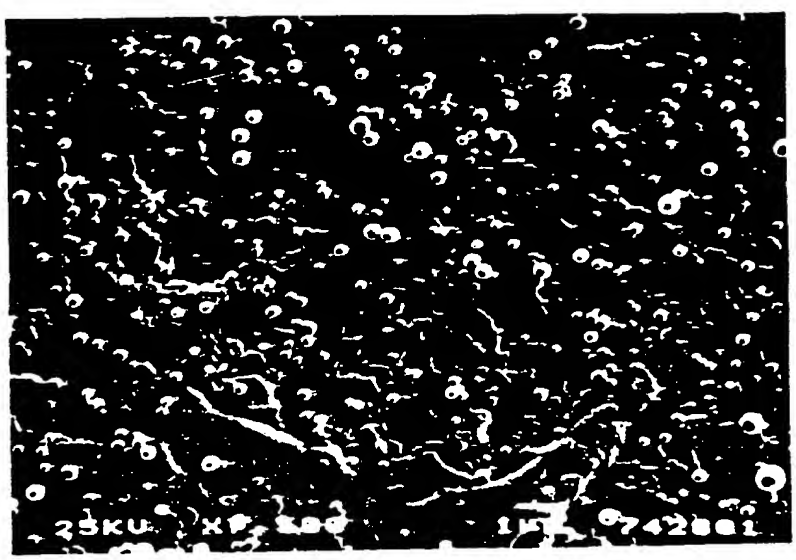


FIG. 3

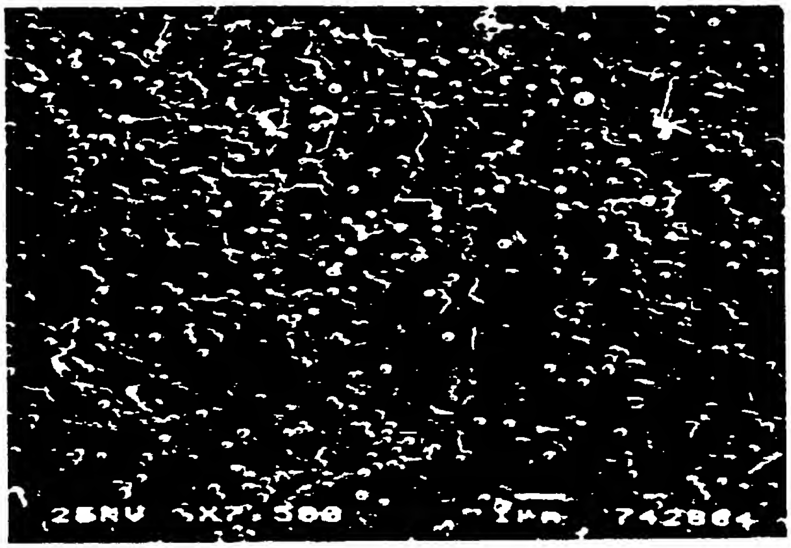


FIG. 4

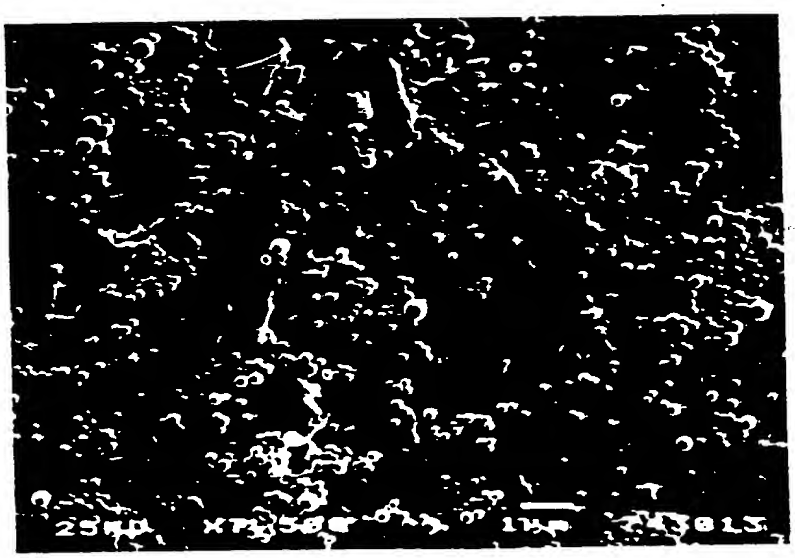


FIG. 5

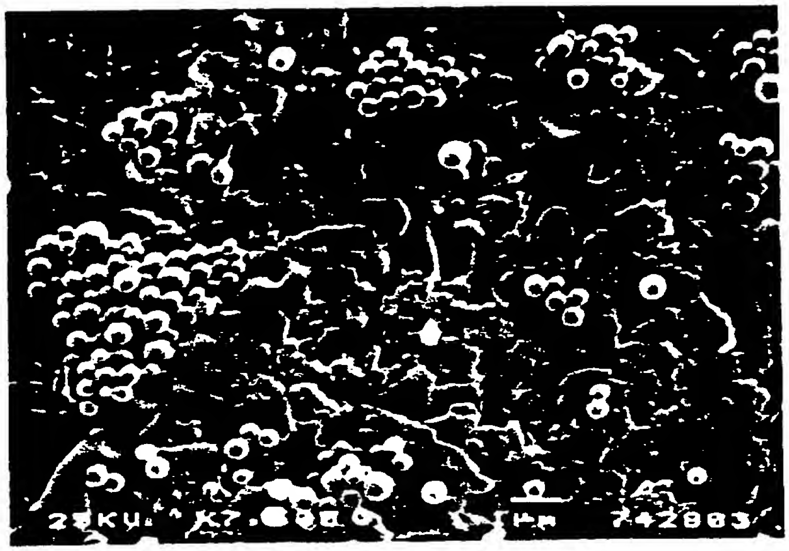


FIG. 6

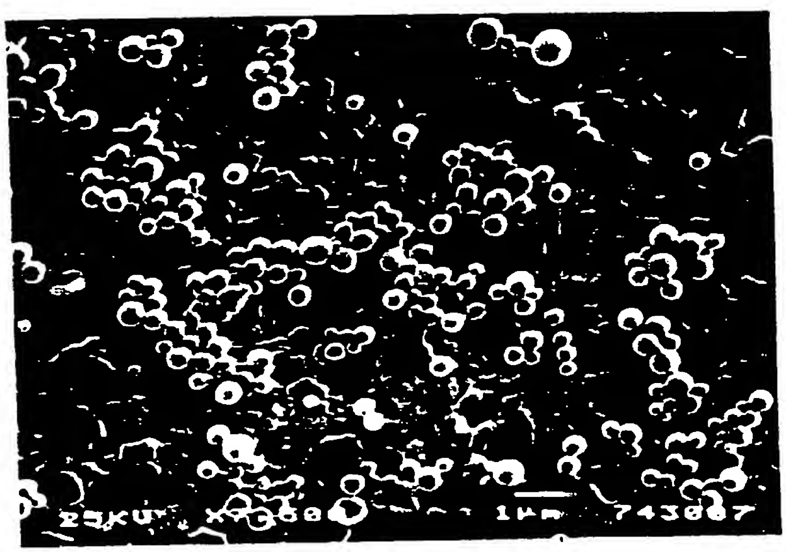


FIG. 7

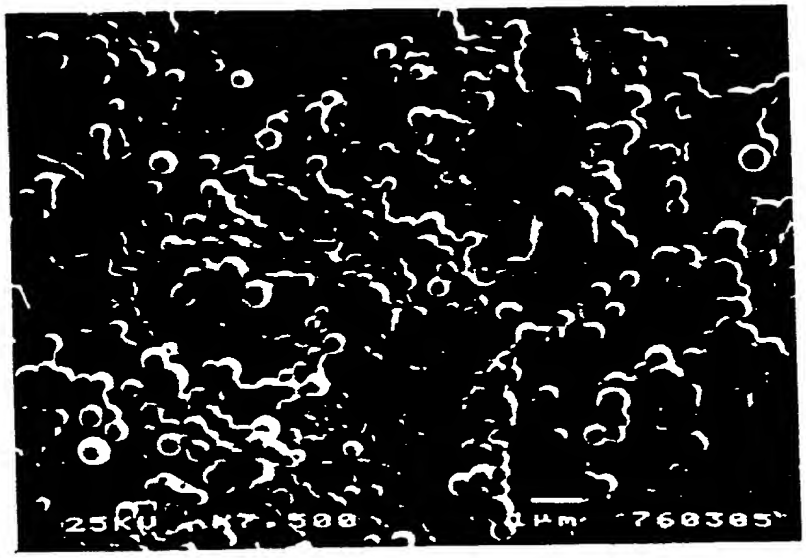


FIG. 8

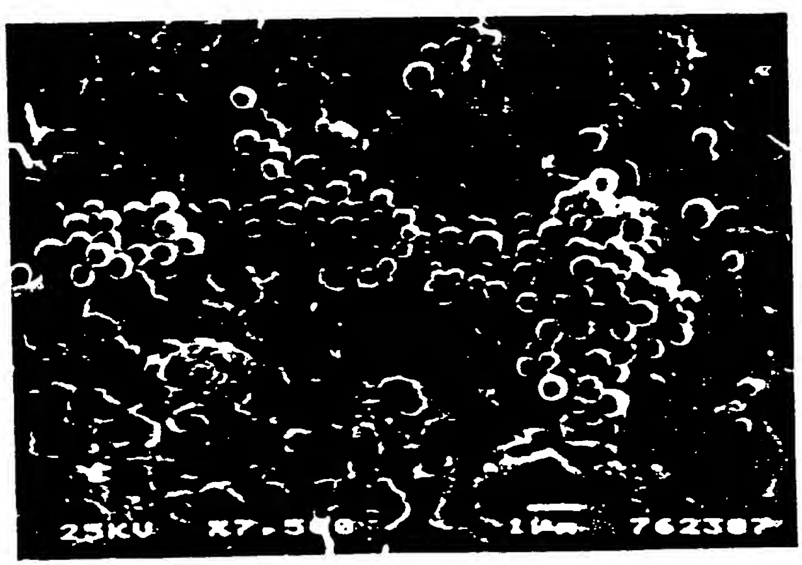
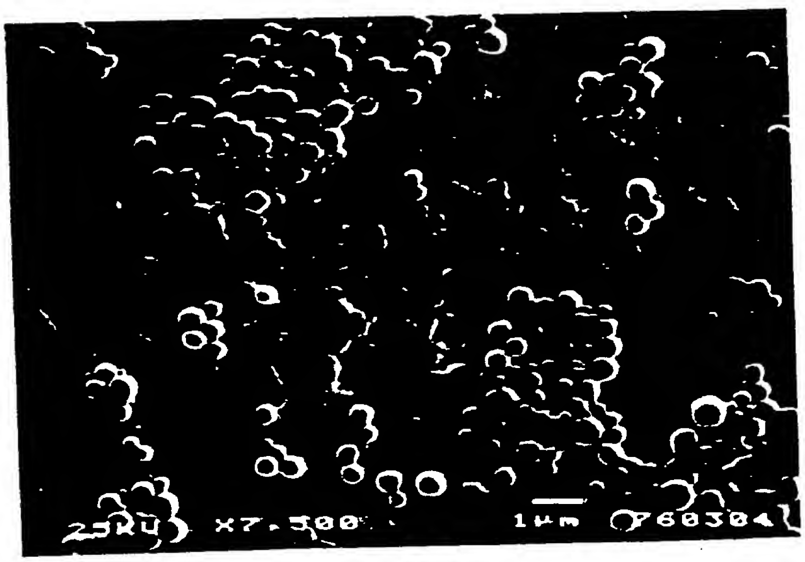


FIG. 9



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EUROPEAN SEARCH REPORT

Application Number

EP 87 11 4541

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-2 833 737 (J.G. MARK et al.) * Claim 1; column 3, lines 58-69; column 4, lines 8-13 *	1-8,10-18	C 08 F 18/08
X	US-A-2 581 844 (W. EGGLESTON) * Claims 1,3; example 1 *	1,2,6, 10-18	
A	US-A-2 965 623 (H. WECHSLER et al.) * Claim 1 *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 08 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24-06-1988	CAUWENBERG C.L.M.

CATEGORY OF CITED DOCUMENTS

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